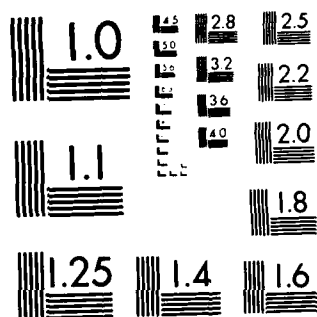


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1. REPORT NUMBER <u>ARO 21828.1-MS-S</u>	2. GOVT ACCESSION NO. <u>N/A</u>	3. RECIPIENT'S CATALOG NUMBER <u>N/A</u>
4. TITLE (and Subtitle) <u>A NEW PROCESS FOR SYNTHESIS OF SILICON NITRIDE POWDERS FOR ADVANCED CERAMICS</u>		5. TYPE OF REPORT & PERIOD COVERED <u>Final Report</u> <u>17 Sept 1984 - 16 Sept 1987</u>
7. AUTHOR(s) <u>D.B. Olson and H.F. Calcote</u>		6. PERFORMING ORG. REPORT NUMBER <u>AeroChem-TP-469</u> ✓
PERFORMING ORGANIZATION NAME AND ADDRESS <u>AeroChem Research Laboratories, Inc.</u> <u>P.O. Box 12</u> <u>Princeton, NJ 08542</u>		8. CONTRACT OR GRANT NUMBER(s) <u>DAAG29-84-C-0023</u>
CONTROLLING OFFICE NAME AND ADDRESS <u>U. S. Army Research Office</u> <u>Post Office Box 12211</u> <u>Research Triangle Park, NC 27709</u>		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE <u>November 1987</u>
		13. NUMBER OF PAGES <u>23</u>
		15. SECURITY CLASS. (of this report) <u>Unclassified</u>
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
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19. KEY WORDS (Continue on reverse side if necessary and identify by block number) <u>Ceramic powders; flames; ignition; silicon nitride; synthesis</u>		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) <u>A new self-sustaining flame synthesis process for producing improved silicon nitride powders was experimentally tested. Mixtures of silane and ammonia could not be ignited, but mixtures of silane and hydrazine or silane, ammonia, and hydrazine were found to support stable flames over a wide range of pressures and reagent ratios. Flames with less than the stoichiometric amount of silane produced fine, white, amorphous powders of silicon nitride with specific surface areas from 90-150 m²/g and intrinsic densities of about 3.0 g/cm³.</u> (over)		

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Yields greater than 90% and production rates of greater than 10 g/min were achieved. X-ray analysis, infrared spectra, and emission analysis for metals confirmed the material to be high purity. Samples typically contained 3% oxygen which was probably introduced in handling.

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I. INTRODUCTION

This research program was performed to evaluate the use of a continuous, self-sustaining flame reaction route to produce fine, uniform, high purity silicon nitride powders and to evaluate the potential of such powders for making improved advanced ceramic materials. The results of this investigation indicate that there is a high probability that the new process can be used successfully on both laboratory and commercial scales to produce such Si_3N_4 powders.

The generation of fine, ultrapure, uniform, spherical, loosely agglomerated particles is currently of intense interest because of their recognized¹ properties as suitable starting materials for producing high performance, dense ceramic articles. The densified bodies produced from such powders are predicted to have high strength and significantly enhanced reproducibility^{1,2} of fabrication. Direct synthesis of these ceramic powders from gas phase reactants is a promising route for achieving the desired properties.¹⁻⁸ The ideal gas phase process would cause rapid particle-forming reactions to occur in a region of controlled reagent concentrations, thus minimizing nucleation and growth times (hence yielding small particles with a narrow size distribution). These conditions can be realized by providing a sharp thermal gradient in a flowing reactant mixture. This has been done using lasers,^{3,9} RF plasma heating,^{10,11} heated flow tube reactors,¹²⁻¹⁴ and now with the flame process. An additional advantage of such gas phase methods over other methods, such as chemical vapor deposition or solid state synthesis, is the avoidance of contact of the reactants or products with walls where contamination often occurs.

Flames are widely used¹⁵ as synthesis reactors for producing fine particles such as carbon black, titanium dioxide, and silica. The flame system that we have discovered for synthesizing ceramic powders shares the advantages of other gas phase synthesis methods but avoids some of their disadvantages. One important advantage is simplicity, which leads to direct scalability and low process equipment costs, an advantage over laser-based methods. There is no fundamental limit on the amount of gas that can be converted to solid product using a large flame or series of small flames. Compared to plasma heating, flame synthesis is a milder process with a much better defined temperature, pressure, and composition history. Compared to heated flow tube reactors, flame synthesis provides a much more compact reaction zone, higher throughput, more uniform conditions, and it eliminates wall interactions.

For a chemical system to support a self-sustaining reaction, thermodynamic and reaction kinetic factors must combine to allow enough energy release to raise the temperature of the products such that feedback of heat and reactive intermediate species from the products to the reactants will maintain the reaction front against the flow of reagents. Figure 1 depicts one type of self-sustaining reaction system, a flat one-dimensional flame, such as might be produced above a multitubular burner through which premixed reagents are fed. At an appropriate linear flow rate of reactants, called the "burning velocity," the flame will remain stationary above the tube bundle. In practice, considerable leeway in flow rate is possible because of stabilization by heat transfer to the burner. The primary reaction zone is usually thin, typi-

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cally 0.1 cm, for a hydrocarbon/air mixture at 100 kPa, corresponding to a flow time of about 1 ms.

Flames have some limitations as chemical reactors. Reagent concentrations cannot be varied completely at will since sufficient reactive species concentrations are needed to drive the reactions, i.e., some reagent ratios will not support continuous reaction. Reaction temperature and temperature profiles through the flame are also constrained by the reactant concentrations and the thermodynamic characteristics of the system. Some control over these factors can be exercised by the use of diluents, by altering the amount of energy lost or added to the system, by varying the pressure, and by varying the type of flame.

II. RESULTS AND DISCUSSION

A. THERMODYNAMIC EQUILIBRIUM CALCULATIONS

The starting point in defining a flame system is the thermodynamic properties which drive the flame reactions. For the present work, the three reactant species of interest are silane, ammonia, and hydrazine (SiH_4 , NH_3 , and N_2H_4). The equilibrium adiabatic reaction temperature at atmospheric pressure of a mixture of SiH_4/NH_3 in a 3/4 mole ratio is 1590 K with 100% conversion of silicon from SiH_4 into Si_3N_4 . Figure 2 shows the variation of calculated reaction temperatures and yields with input reagent ratios at atmospheric pressure. Equivalence ratio is defined for SiH_4 and NH_3 mixtures as:

$$\phi = \frac{(\text{SiH}_4/\text{NH}_3)_{\text{mix}}}{(\text{SiH}_4/\text{NH}_3)_{\text{stoichiometric}}}$$

where $(\text{SiH}_4/\text{NH}_3)_{\text{stoichiometric}}$ is defined as the stoichiometric reagent ratio for the reaction $3\text{SiH}_4 + 4\text{NH}_3 = \text{Si}_3\text{N}_4 + 12\text{H}_2$. The reaction temperature is a maximum at the stoichiometric reagent ratio and the silicon nitride yield (based on silicon) is 100% for equivalence ratios of one or less. At higher equivalence ratios there is insufficient nitrogen to convert all of the silicon into silicon nitride, and the yield is less than 100%. Similar calculated flame temperature and percentage yield data for SiH_4 reacting with hydrazine are shown in Fig. 3 at four reaction pressures. Equivalence ratio is defined for SiH_4 and N_2H_4 mixtures as:

$$\phi = \frac{(\text{SiH}_4/\text{N}_2\text{H}_4)_{\text{mix}}}{(\text{SiH}_4/\text{N}_2\text{H}_4)_{\text{stoichiometric}}}$$

where $(\text{SiH}_4/\text{N}_2\text{H}_4)_{\text{stoichiometric}}$ is defined as the stoichiometric reagent ratio for the reaction $3\text{SiH}_4 + 2\text{N}_2\text{H}_4 = \text{Si}_3\text{N}_4 + 10\text{H}_2$. It can be seen that the reaction temperature peaks at an equivalence ratio of about 0.5, reflecting the heat release from excess N_2H_4 decomposition, and increases with increasing system pressures. All of the calculated temperatures are sufficient to expect these reagents to support a flame. The yields exceed 98% only for equivalence ratios of less than about 0.2 except for the 508 kPa calculation where > 98% yield is obtained at equivalence ratios up to about 0.5. In cases where the silane conversion to Si_3N_4 yield is less than 100%, the excess silicon is calculated to be converted into free silicon.

B. IGNITION AND PROPAGATION EXPERIMENTS

The second step in defining a flame system is the experimental determination of its ignition characteristics as a function of reagent mixture ratio, initial temperature, pressure, etc. The ignition properties of mixtures of SiH_4 and NH_3 were investigated initially to see if they would support a flame and produce silicon nitride. The experiments were done in a static ignition bomb, Fig. 4, with cylindrical internal volume of 160 cm³ (8.6 cm length, 4.8 cm diam) designed to operate up to pressures of about 10 MPa at 530 K. Chromel, tungsten, or tungsten/rhenium fuse wires were used to ignite the mixtures and ignition, when it occurred, was detected by an increase in pressure and by the solid product remaining in the reaction chamber. To shake down the apparatus, several initial experiments were performed using acetylene decomposition at elevated pressure; the results were consistent with previous work.¹⁶

Mixtures of SiH_4 and NH_3 did not ignite under the following range of experimental conditions: total pressure = 10 to 1420 kPa (0.1 to 14 atm), initial temperature = 300 to 400 K, fuse wire ignition energies from ~ 1 to 4 J, wire fusion times from ~ 1 to 10 ms, and reagent equivalence ratios, ϕ = 0.4 to 1.5. In some experiments, although no significant pressure rise was observed, a coating of fine, tan colored powder was found on the ignition wire holders after the experiments. Apparently the reaction was initiated but failed to propagate.

It is not clear why SiH_4/NH_3 mixtures do not ignite. Pyrolysis experiments with SiH_4/NH_3 mixtures to produce silicon nitride have been done¹⁴ in flow tubes where the total reactant mixture was heated to 750 to 1200 K. The adiabatic flame temperature for SiH_4/NH_3 is calculated to be higher than this temperature range; possibly the reaction rates are too slow at these temperatures to support flame propagation. Several other chemical systems, some producing solid products, support flames with comparable or lower calculated flame temperatures: e.g., propyne (1580 K); 3-methylbutyne-1,ene-3 (1150 K); and hydrazine (1100 K). To overcome this inability to achieve ignition, the reaction system was changed to include N_2H_4 or $\text{N}_2\text{H}_4/\text{NH}_3$ mixtures. Hydrazine can be ignited alone in a decomposition flame at 20 kPa with 90 mJ of ignition energy.

Ignition was achieved in the bomb apparatus with $\text{SiH}_4/\text{N}_2\text{H}_4$ mixtures over a wide range of conditions from an equivalence ratio of 0.0 (hydrazine decomposition) to greater than stoichiometric. Since these mixtures could be ignited at pressures less than atmospheric, ignition/propagation measurements

were made in a cylindrical Pyrex tube reactor, 10 cm diam by 41 cm length, with a similar fuse wire ignition system. Ignition was achieved at pressures as low as 20 kPa. Solid product was collected and weighed. At equivalence ratios of less than 0.7, the solid product mass was greater than 90% of the theoretical Si_3N_4 mass and greater than the total Si mass.

Further ignition experiments were conducted with NH_3 added to the $\text{SiH}_4/\text{N}_2\text{H}_4$ mixtures in the Pyrex reactor. Ignition was achieved over a range of compositions at pressures down to 40 kPa. These experiments showed that, over an equivalence ratio range of 0.3 to 1.6 (lean to rich in silane), ignition limits increased with increasing $\text{N}_2\text{H}_4/(\text{N}_2\text{H}_4 + \text{NH}_3)$ ratio and equivalence ratio as shown in Fig. 5. Equivalence ratio is defined for $\text{SiH}_4/\text{N}_2\text{H}_4/\text{NH}_3$ mixtures as:

$$\phi = \frac{(\text{SiH}_4/(\text{N}_2\text{H}_4 + \text{NH}_3/2))_{\text{mix}}}{(\text{SiH}_4/\text{N}_2\text{H}_4)_{\text{stoichiometric}}}$$

The circles in Fig. 5 represent "non-ignition" mixtures and the squares represent "ignition" mixtures. For $\phi = 0.2$ and 1.6, ignition was obtained for mixtures with $\text{N}_2\text{H}_4/(\text{N}_2\text{H}_4 + \text{NH}_3)$ ratios as low as 16% and 36%, respectively, independent of pressure (30 to 100 kPa). The ignition limits were relatively independent of total initial pressure from about 40 to 100 kPa. For $\phi = 0.5$ mixtures at 100 kPa, a desirable operating pressure, the calculated adiabatic flame temperature is 1990 K and the theoretical yield is ~ 88% (based on silicon conversion). The yield is calculated to increase at lower equivalence ratios or at lower temperatures which could be obtained by diluting with inert gas.

Solid product samples were collected from tests made at a total initial pressure of 65 kPa, $\text{NH}_3/\text{N}_2\text{H}_4 = 1.7$, and an overall $\phi = 0.6$. The adiabatic flame temperature for this mixture is 1750 K and the theoretical yield 95%. The recovered solid sample mass indicated that close to this yield was obtained. Samples were subjected to selected tests at Rutgers University by Professor Stephen Danforth (whose laboratory performed all x-ray, FTIR, and annealing tests on products from this program discussed in this report). X-ray diffraction showed the sample to be amorphous or microcrystalline with particle size estimated to be less than 5 to 10 nm in diameter. The sample remained amorphous after annealing in argon at 100 kPa and 1670 K for 1.5 h. This indicates the sample contained no free silicon; because free silicon would have crystallized at this temperature. Another sample from the same experiment crystallized on annealing at 1750 K for 1 h in argon. X-ray diffraction indicated a silicon-free material with $\alpha\text{-Si}_3\text{N}_4$ four to five times more prevalent than $\beta\text{-Si}_3\text{N}_4$. Silicon oxynitride ($\text{Si}_2\text{N}_2\text{O}$) was also present; this could have come from exposure to air or from water in the hydrazine. From these data it was concluded that the sample was Si_3N_4 , with good purity.

These ignition and propagation experiments therefore provided the foundation to expect flames of SiH_4 , N_2H_4 , and NH_3 to be stable and to produce Si_3N_4 .

C. CONTINUOUS FLOW REACTOR STUDIES

1. Apparatus

The next phase of the program was to utilize a burner to stabilize a continuous, self-sustaining flame to produce material under a more nearly steady-state condition and to produce larger product samples. The apparatus was designed to house various sized burners, use both N_2H_4 and NH_3 , collect large samples, and exclude air. Hydrazine is toxic but fairly safe in the liquid phase; however, due to its monopropellant characteristic in the vapor phase it can decompose explosively if ignited. The ignition limits for mixtures of N_2H_4 in NH_3 were therefore determined as a safety guide for handling these mixtures in the continuous flow feed system. The results are shown in Fig. 6. Mixtures containing greater than 40 mole percent N_2H_4 could be ignited from about 50 to 100 kPa at an initial temperature of 420 K. The reactant feed system was therefore designed to dilute the vaporized hydrazine with N_2 or NH_3 to reduce the danger.

The first experiments, performed using tubular Bunsen burners, were troubled by ignition difficulties. Mixture compositions ignitable in the Pyrex reactor did not support a continuous flame, probably due to hydrazine decomposition on surfaces, especially the heated stainless steel flow lines for hydrazine vapor feed. These were replaced by Teflon lines and most other stainless steel parts were replaced by aluminum, both of which are more compatible with N_2H_4 . With these changes, a $\phi = 0.25$ mixture of $SiH_4/N_2H_4/N_2$ was ignited in a 2.5 cm diam, 36 cm long single tube Pyrex burner at an unburned gas velocity of 16 cm/s. The flame burning velocity was too high to maintain a stationary flame front, so the flame was repeatedly (about 150 times) ignited at one end and allowed to propagate up the glass tube. A fine, pure white powder was collected. The surface area of this powder was measured by nitrogen BET to be 170 m^2/g which corresponds to a particle diameter of about 13 nm, assuming a density of 2.8 g/cm^3 . The sample, as prepared, was amorphous as demonstrated by X-ray analysis.

The apparatus was then changed to produce a flat flame in order to stabilize flames with various burning velocities. The apparatus consisted of a 2.7 cm diam burner made up of about 350 stainless steel tubes, each with i.d. = 0.08 cm, on which a flat, premixed flame could be stabilized. The burner was surrounded by an annulus of 4.6 cm o.d. comprised of similar individual tubes through which nitrogen flowed to form a shroud. The nitrogen flow velocity was adjusted to about the same velocity as the reactant/product gases. The shroud flow serves both to maintain the integrity of the reacting flow stream and to keep the newly formed particles from reaching the process vessel wall. Ignition was achieved with an electric spark. The particles were collected by spraying a liquid, e.g., water or a hydrocarbon such as isooctane, into the exhaust gas/particle flow downstream of the flame. Collecting the particles using a liquid spray eliminates the pressure drop usually encountered when a filter is used, makes the product easier to handle and minimizes exposure to oxygen. The collected product was periodically removed by opening a drain valve and transferring the slurry into a bottle. The filled bottle could then be sealed, removed, and another connected to the apparatus. In this manner the flat-flame burner apparatus could be run continuously.

2. Ranges of Operation

Experiments were performed in which the reagents, $\text{SiH}_4/\text{NH}_3/\text{N}_2\text{H}_4/\text{N}_2$, and the total gas feed velocity were varied over large ranges. The flames are stable over a remarkably wide range of process conditions. Varying the reagent composition, of course, varies the temperature of the flame, in this case from 1170 to 1765 K (calculated adiabatic equilibrium flame temperatures). Powders were prepared by drying the slurry, and various properties of the powders were measured. The ranges of conditions studied on this apparatus are shown in Figs. 7-9. In Fig. 7, each point or line (where the conditions were varied during one experiment) represents the values of the equivalence ratio and $\text{N}_2\text{H}_4/(\text{N}_2\text{H}_4 + \text{NH}_3 + \text{N}_2)$ ratio for an experiment. Figure 8 shows the unburned gas velocities which gave stable flames on this burner, and Fig. 9 presents the calculated adiabatic flame temperature for each flame. These data demonstrate that a wide range of conditions gave stable flames: $0.0 \leq \phi \leq 1.0$, $\text{N}_2\text{H}_4/(\text{N}_2\text{H}_4 + \text{NH}_3 + \text{N}_2) = 0.5$ to 0.13 , with unburned gas velocities from about 30 to 150 cm/s. These data do not indicate that flames are necessarily unstable outside of the ranges shown, just that the range of stable flames is at least this large. Several experiments were run at Si_3N_4 production rates of 10 g/min which showed yields of roughly 90% of theoretical.

3. Product Characteristics

The powders produced from these flames of $\text{SiH}_4/\text{N}_2\text{H}_4/\text{NH}_3/\text{N}_2$ are pure white to tan depending on process conditions, have specific surface areas in the 90-150 m^2/g range, are amorphous Si_3N_4 as produced, and crystallize to $\approx 100\%$ α -phase upon annealing at 1870 K. Heating dry powder in air to 1275 K showed no color or surface area change with $0 \pm 4\%$ weight change. A thermogravimetric analysis of one sample, run at Rutgers University, was flat to 1275 K. The variation from white to tan in the various materials is probably caused by the increasing amounts of silicon. Fourier transform infrared spectra of white amorphous powder, as shown in Fig. 10, indicated pure silicon nitride. Small impurity peaks due to Si-O and Si-OH were also observed; the sample was handled in air. Annealing at 1750 K in argon did not change the spectra. On average, the powder surface area was $\approx 120 \text{ m}^2/\text{g}$ and the gas displacement particle density was $\approx 3.0 \text{ g/cm}^3$, giving an equivalent average spherical particle diameter of 17 nm. Particle diameters have varied from about 10 to 50 nm as estimated by this technique. Si_3N_4 powder properties are affected by variations in reagent ratios, dilution, and flame temperature.

Scanning electron micrographs of one cluster of ≈ 200 primary particles showed the primary particles to be spherical with no porosity visible. No information on the strength of agglomeration was obtained.

Powders dried from slurry have a tap density of $\approx 0.35 \text{ g/cm}^3$. Pellets of pure, dry powder pressed to 69 MPa showed green densities of 25 to 35% of theoretical density. At 173 MPa, pellet densities of 40 to 45% of theoretical were obtained. Curves of green pellet density vs. log (applied pressure), Fig. 11, show a sharp increase in slope at $\approx 15 \text{ MPa}$. We interpret these experiments as indicative of the strength of the agglomerates. Compaction tests of low oxygen exposure powders showed similar behavior to samples handled in air. Adding dispersant to the hydrocarbon slurry prior to drying the powder

was found to yield green compacts with somewhat higher densities compared to the same material without dispersant, probably due to a reduction of the degree or strength of agglomeration. This and other improved powder processing techniques should yield green compacts with higher densities and uniformity. The quality of the green compact is critically important in determining the performance of the densified end product since any void or dislocation is amplified upon sintering. The quality of the initial powder is a key factor in determining the characteristics of the green compact, and therefore, ultimately of the end product.

A potential problem with this flame apparatus was that Si_3N_4 was deposited on the burner surface during operation. This material remained exposed to reagents and high temperatures for long periods of time, and some may subsequently have entered the product slurry. Since this deposit material, which has a greatly reduced surface area, $\approx 5 \text{ m}^2/\text{g}$, appears to be strongly agglomerated, its presence may have detracted from the properties of the product. An improved design is needed to prevent these deposits from forming and adhering to the burner or at least to prevent their entering the collected product.

4. Impurities

Si_3N_4 powder samples produced with water spray collection and handled in air were found to contain considerable oxygen. This is not surprising since the powders have a large, probably highly reactive surface area which could react chemically with either water or molecular oxygen. One sample, collected and stored in water, showed an oxygen content of about 25% and a particle density of 2.3 g/cm^3 . To minimize oxygen contamination, the use of water was discontinued, the reactor was upgraded to allow slurry to be removed without exposure to air, and a nitrogen atmosphere dry-box was set up to handle samples and filter slurry.

The intrinsic particle density, measured by He displacement, of a powder with large oxygen fraction would be expected to be significantly lower than for pure Si_3N_4 (the density of α -phase is 3.18 g/cm^3 , but that of amorphous may be $\approx 2.9\text{-}3.1 \text{ g/cm}^3$). Indeed, the air and water exposed samples were found to have densities of about $2.4\text{-}2.6 \text{ g/cm}^3$, whereas densities of samples collected in acetonitrile or hydrocarbon and without air exposure had densities of $2.9\text{-}3.1 \text{ g/cm}^3$. Samples with and without air exposure were analyzed for oxygen content by neutron activation analysis. Samples with the least exposure to residual air still showed around 3% (weight) oxygen, while samples which were exposed to air by pouring and filtering the hydrocarbon/powder slurry outside of the dry box, showed 4-5% oxygen.

Emission spectroscopic analysis of initial samples for metal impurities gave large values for copper (100-1000 ppm) and aluminum (10-100 ppm) contents. The sources of these contaminants were probably the materials of construction of the reactor, so modifications were made to remove most brass and aluminum items. A spray Teflon coating was applied to the inner surfaces of the aluminum hydrazine vaporizer and the brass burner housing. Emission spectroscopic analyses of samples produced subsequent to these modifications showed small amounts of aluminum, iron, copper, and magnesium. The sum of these metal impurity concentrations was less than 100 ppm (weight). Not de-

tected with a 10 ppm instrumental sensitivity were 17 other metals including chromium, nickel, zinc, lead, tin, and manganese. The remaining impurities probably arise from the brass burner housing and aluminum hydrazine vaporizer. This metal content, < 100 ppm, is considered high purity for silicon nitride.

III. CONCLUSIONS

A new flame synthesis process for producing fine, high purity silicon nitride powders has been experimentally demonstrated. Mixtures of SiH_4 and N_2H_4 or SiH_4 , NH_3 , and N_2H_4 were found to support stable flames over a wide range of pressures and reagent ratios. Atmospheric pressure flames with equivalence ratios of about 0.4 produced fine, white, amorphous powders of silicon nitride with specific surface areas from 90-150 m^2/g and intrinsic densities of about 3.0 g/cm^3 . X-ray analysis, infrared spectra, and emission analysis for metals confirmed the material to be high purity. The simple, small scale flame system used for these studies produced Si_3N_4 powder at rates up to 10 g/min with no significant external energy input.

The powders produced routinely contain < 100 ppm metallic impurities but are highly active and thus contain \geq 3% oxygen impurity. Improvements in the handling procedures and equipment are needed to prevent exposure of the silicon nitride to residual air. Both air and water must be excluded from the reagents and the collection liquid used in slurry processing. Powder uniformity can be improved by eliminating the strongly agglomerated burner deposits from the collected products. An improved burner is needed which would reduce the small recirculation zones present in the current burner between feed tubes to eliminate the source of these deposits. With these improvements, material produced by this new process holds promise as a new source of high purity, fine silicon nitride powders.

IV. LIST OF MANUSCRIPTS SUBMITTED OR PUBLISHED

None. A US Patent Application has been submitted.

V. SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT

The following scientific personnel contributed to this project: H.F. Calcote; D.B. Olson; R.J. Gill; D.G. Keil; W. Felder; L. Aldridge. No degrees were awarded.

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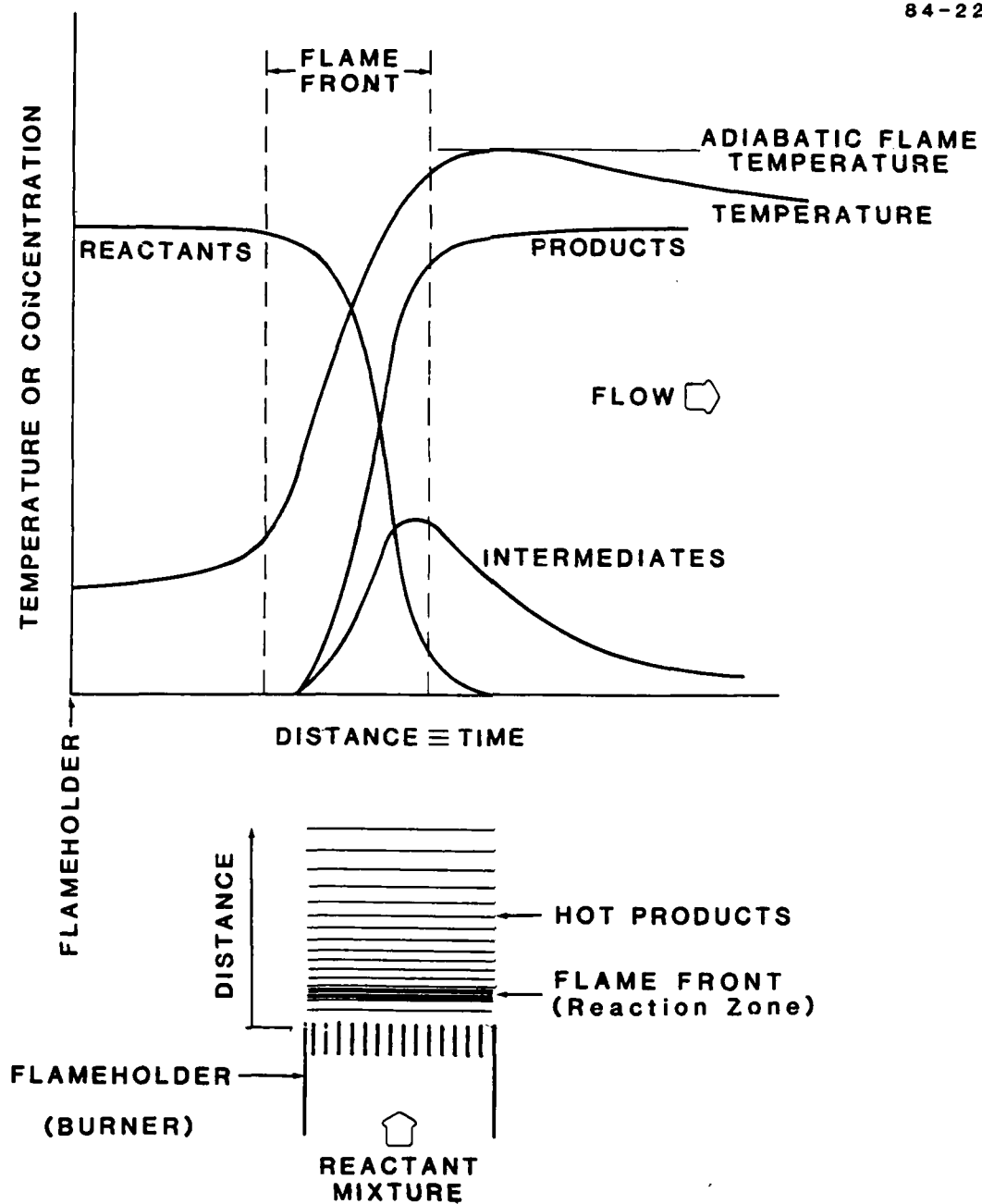


FIGURE 1 A FLAT ONE-DIMENSIONAL FLAME ON A FLAT FLAME BURNER

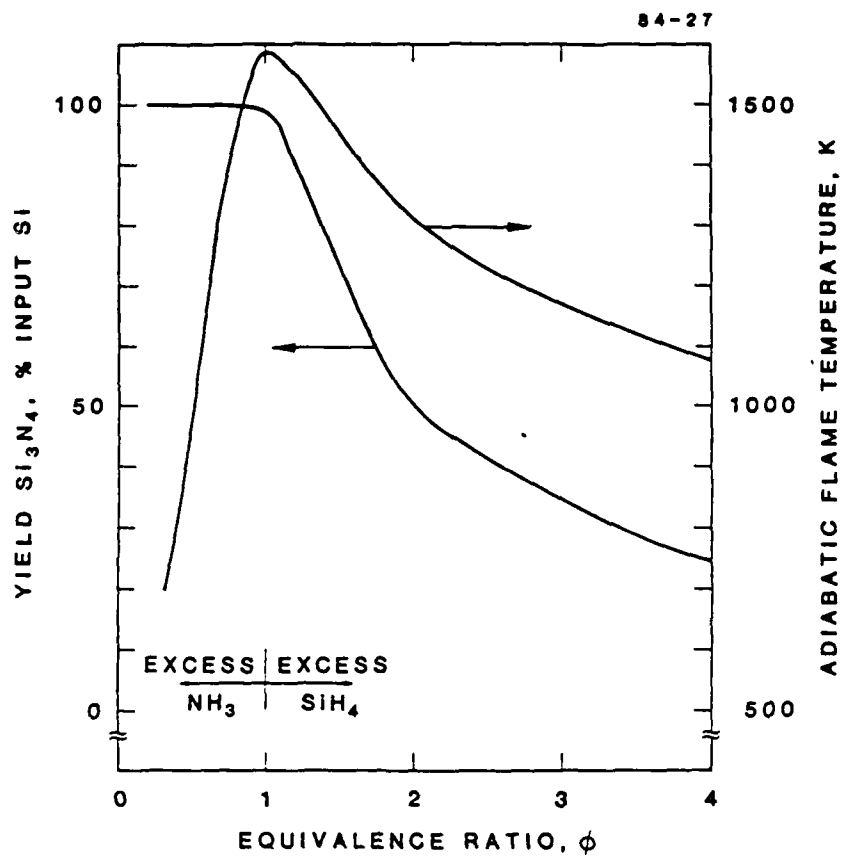


FIGURE 2 YIELD AND ADIABATIC FLAME TEMPERATURE FOR THE REACTION
 $3\text{SiH}_4 + 4\text{NH}_3 \rightarrow \text{Si}_3\text{N}_4 + 12\text{H}_2$ AT 100 kPa

$$\phi = 4/3 (\text{SiH}_4/\text{NH}_3)$$

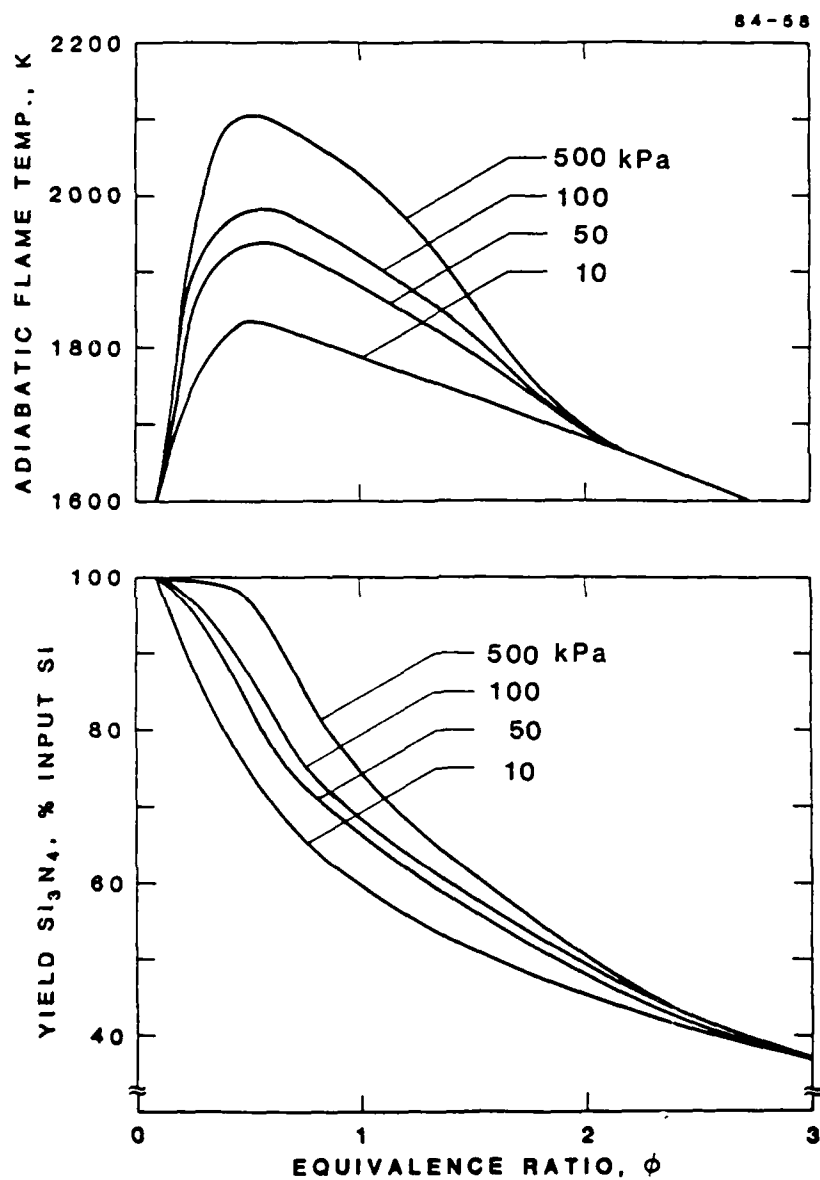


FIGURE 3 YIELD AND ADIABATIC FLAME TEMPERATURE FOR THE REACTION
 $3\text{SiH}_4 + 2\text{N}_2\text{H}_4 \rightarrow \text{Si}_3\text{N}_4 + 10\text{H}_2$

$$\theta = 2/3 (\text{SiH}_4/\text{N}_2\text{H}_4)$$

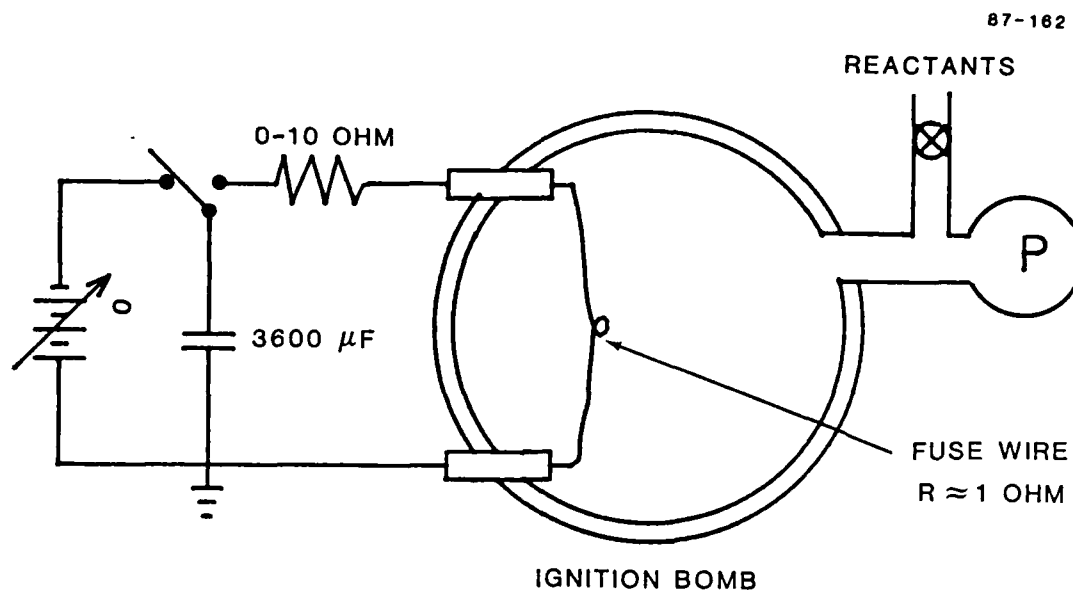
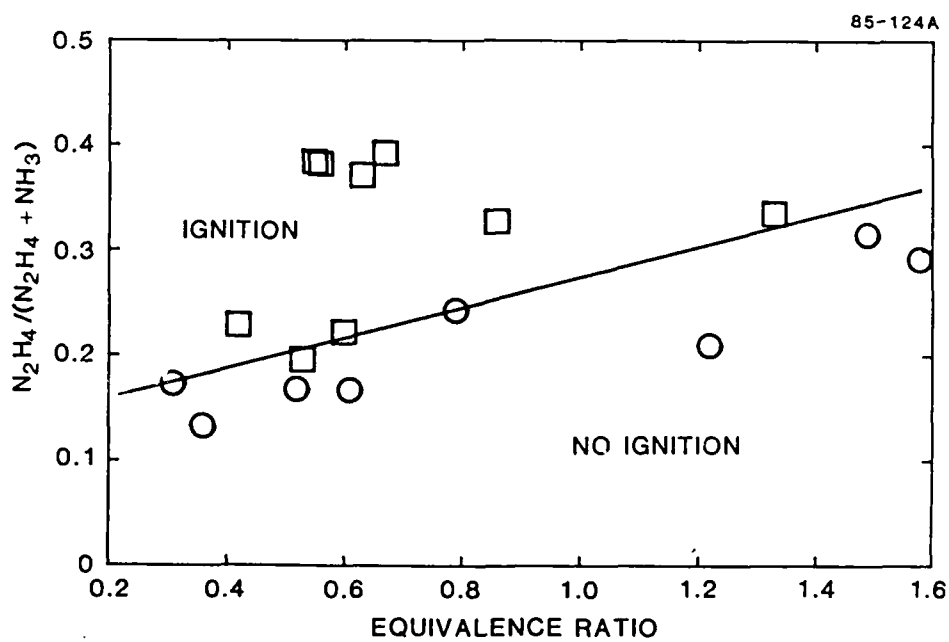
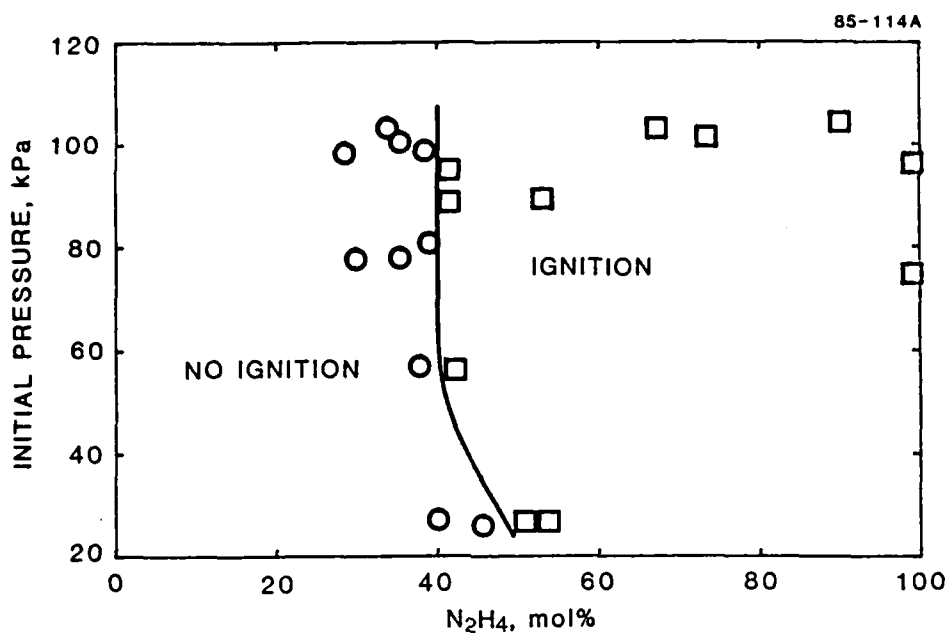


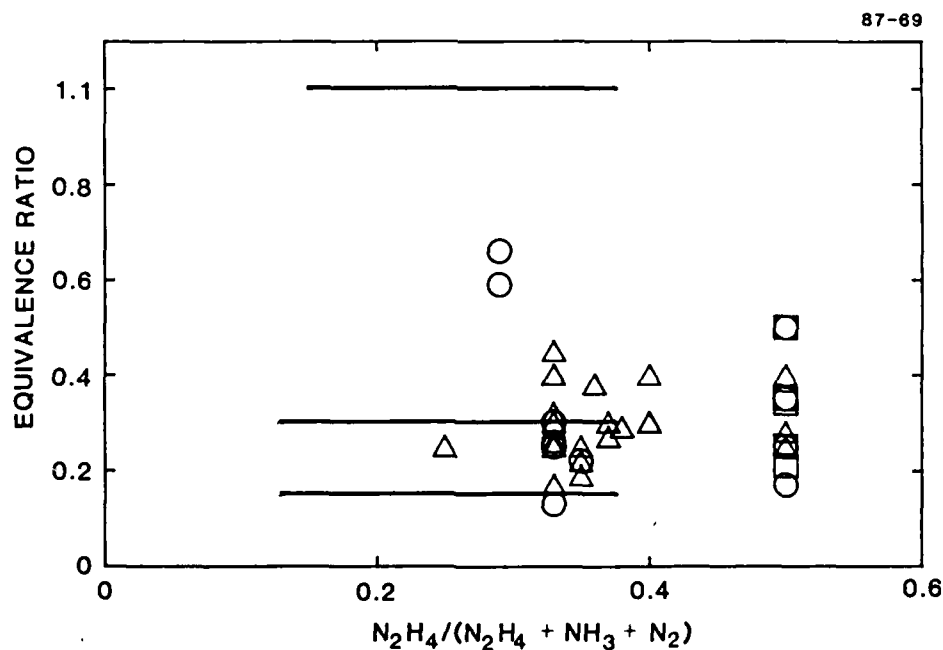
FIGURE 4 SCHEMATIC OF IGNITION BOMB APPARATUS

FIGURE 5 IGNITION LIMITS FOR $\text{SiH}_4/\text{N}_2\text{H}_4/\text{NH}_3$ MIXTURES

□ = ignition; ○ = no ignition

FIGURE 6 IGNITION LIMITS FOR N_2H_4/NH_3 MIXTURES

□ = ignition; ○ = no ignition

FIGURE 7 COMPOSITION OF $SiH_4/N_2H_4/NH_3/N_2$ FLAMES USED TO PREPARE SILICON NITRIDE

Symbols denote product color: ○ = white; △ = off-white to tan; □ = brown. The lines represent experiments in which the flame conditions were varied over the indicated range; the product color was not determined.

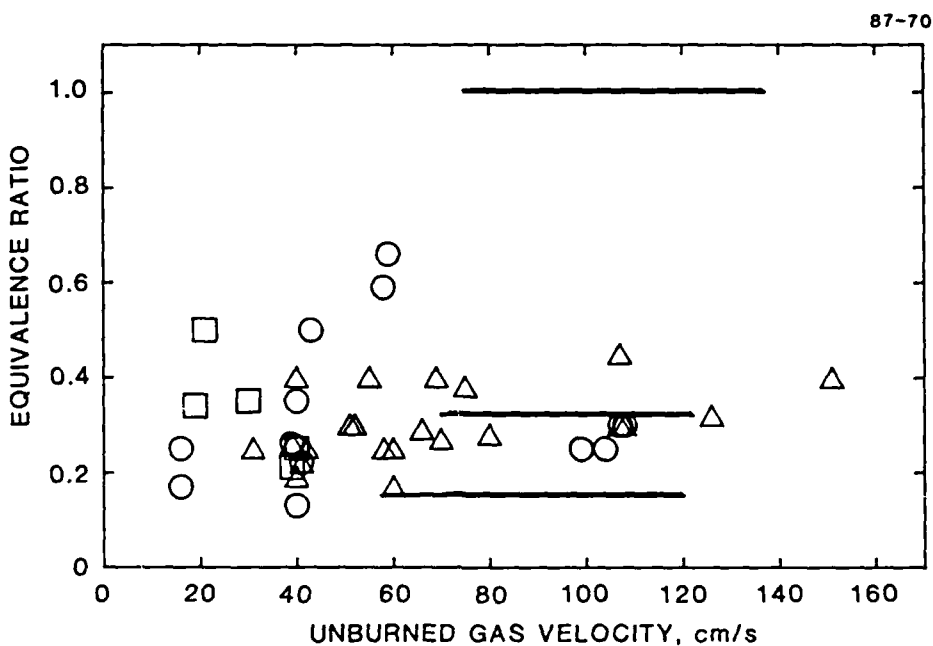


FIGURE 8 EQUIVALENCE RATIOS AND UNBURNED GAS VELOCITIES OF $\text{SiH}_4/\text{N}_2\text{H}_4/\text{NH}_3/\text{N}_2$ FLAMES USED TO PREPARE SILICON NITRIDE

Symbols denote product color: ○ = white; △ = off-white to tan; □ = brown. The lines represent experiments in which the flame conditions were varied over the indicated range; the product color was not determined.

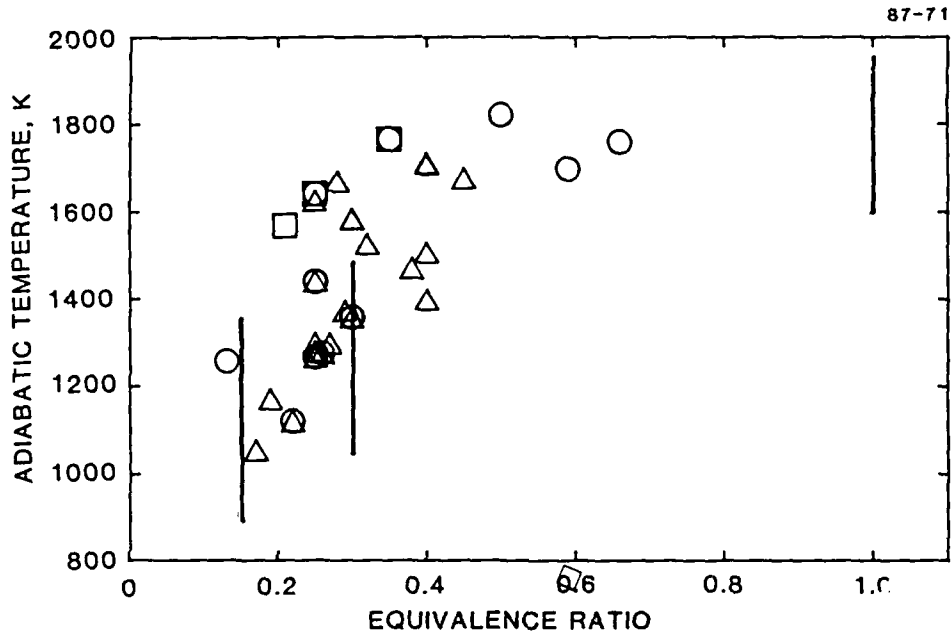


FIGURE 9 ADIABATIC FLAME TEMPERATURE OF $\text{SiH}_4/\text{N}_2\text{H}_4/\text{NH}_3/\text{N}_2$ FLAMES USED TO PREPARE SILICON NITRIDE

Symbols denote product color: \circ = white; \triangle = off-white to tan; \square = brown. The lines represent experiments in which the flame conditions were varied over the indicated range; the product color was not determined.

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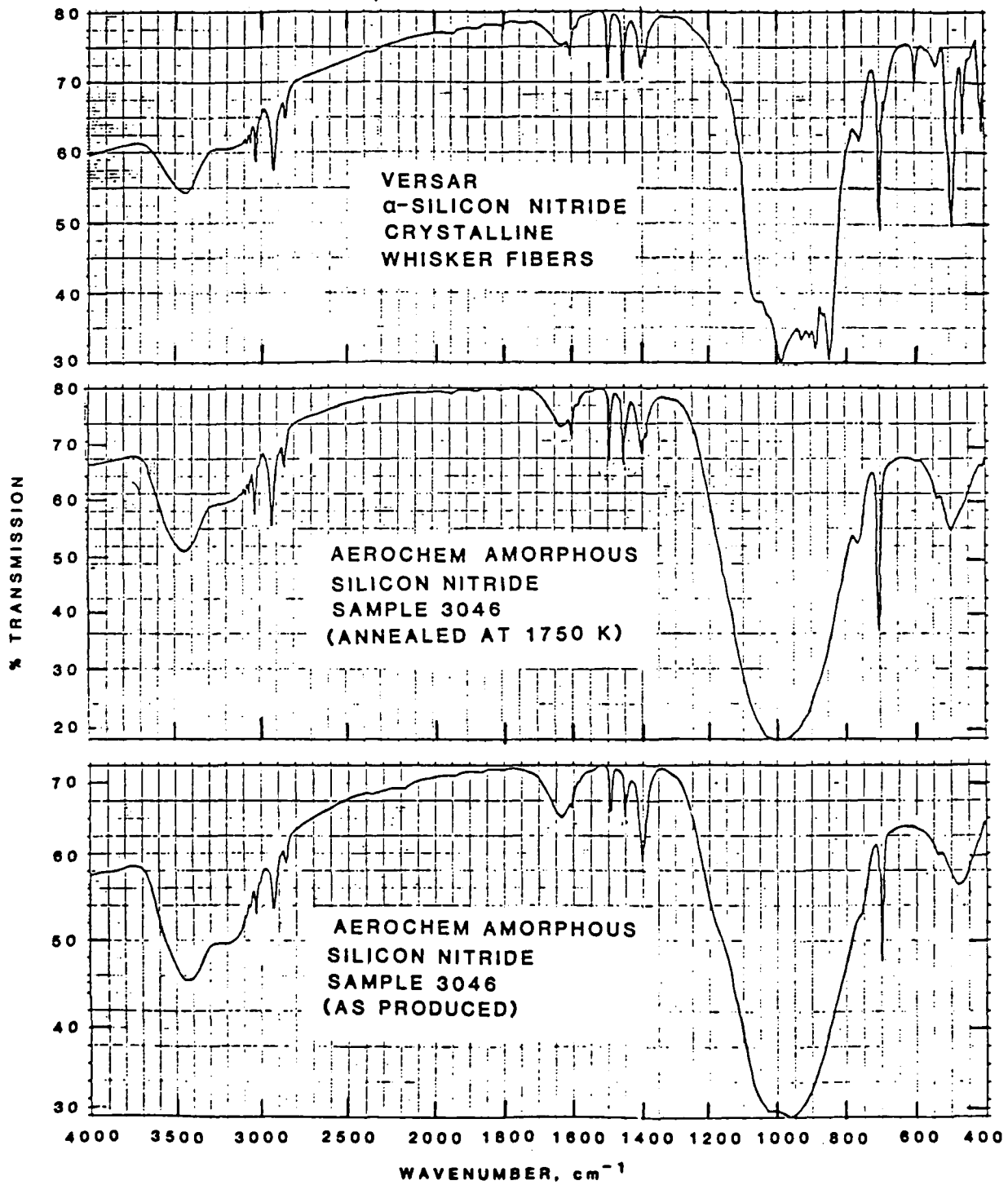


FIGURE 10 INFRARED SPECTRA OF SILICON NITRIDE

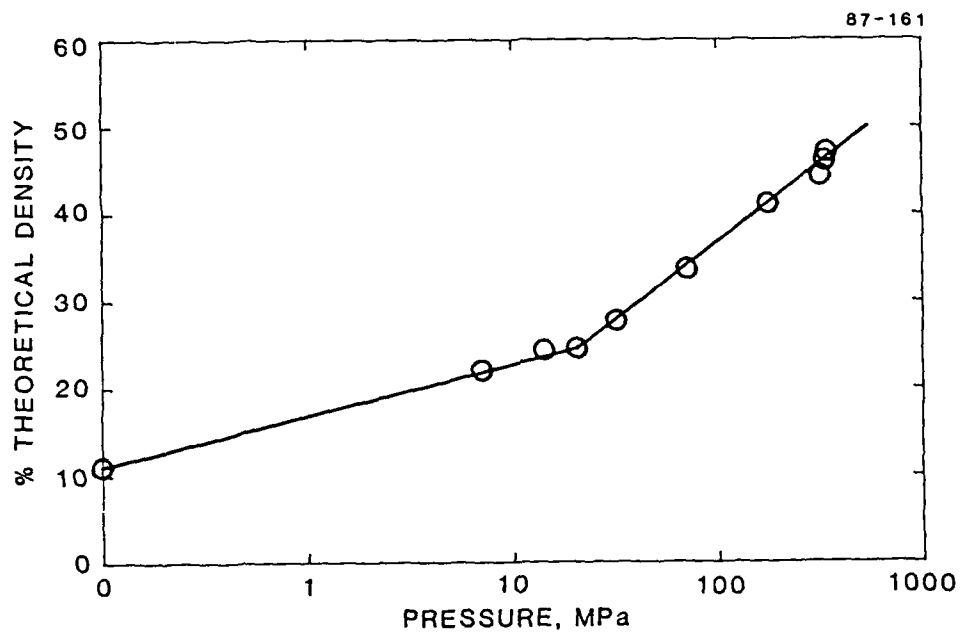


FIGURE 11 COMPACTION TESTS OF SILICON NITRIDE

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